Synthesis Mechanism and Light Influence on unprotected Platinum Nanoparticles Synthesis at Room Temperature

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Abstract: In this communication we present an investigation of the influence of light on the formation of platinum (Pt) nanoparticles (NPs) using standard polyol synthesis reagents at room temperature. It is demonstrated that instead of thermal treatment, UV-light can be used for particle formation thus opening new pathways for the synthesis of NPs with defined size distribution.

The polyol based method for the synthesis of NPs has been shown to be a powerful approach to produce well-defined colloids with narrow size distributions. In several reports it was demonstrated that this method is particularly favorable for an effective and versatile synthesis of Pt-based catalysts [1] and the design of tailored ligand-functionalized NPs.[2] Despite the fact that various types of well-defined, catalytically active Pt and Pt-alloy NPs were obtained [1c], further development of synthesis methods and understanding the size control mechanism is of significance. In order to get more insights into Pt NP formation, we used steady state absorption and fluorescence spectroscopy that provide information on the chemical species present during the particle formation process.

In figure 1 series of UV-VIS absorption and emission spectra are shown monitoring the time evolution of a synthesis reaction mixture while stored at room temperature (RT) and exposed to daylight. As the reaction starts, the first absorption spectrum recorded immediately after creating the reaction mixture by mixing the H_2PtCl_6-EG (hexachloroplatinic acid dissolved in ethylene glycol) and NaOH-EG (sodium hydroxide dissolved in ethylene glycol) solutions indicates the unreduced $PtCl_6^{(-2)}$ complex with an absorption peak at 268 nm, in line with previous reports [3]. At the same time no emission in the 375 – 550 nm range is observed. The 268 nm absorption feature starts to disappear during the first hours while holding the precursor solution at RT, indicating a reaction of the $PtCl_6^{(-2)}$ complex. After a relatively fast stage of the $PtCl_6^{(-2)}$ reaction (~70 hours for complete disappearance), a slow evolution of absorption bands around 305 nm and 360 nm as well as the formation of emissive reaction products appears (with two main excitation bands around 305 nm and 360 nm, see supporting information (SI), Figure S1). In concert with the appearance of new absorption bands after ~350 hours the colloid color gradually changes from light yellow to brownish-yellow, indicating that the growth and formation of Pt NPs has started. Also a broad slope between 250 nm and 450 nm can be seen that increases during the whole reaction and is reported to be related to the formation of Pt NPs as well [4].

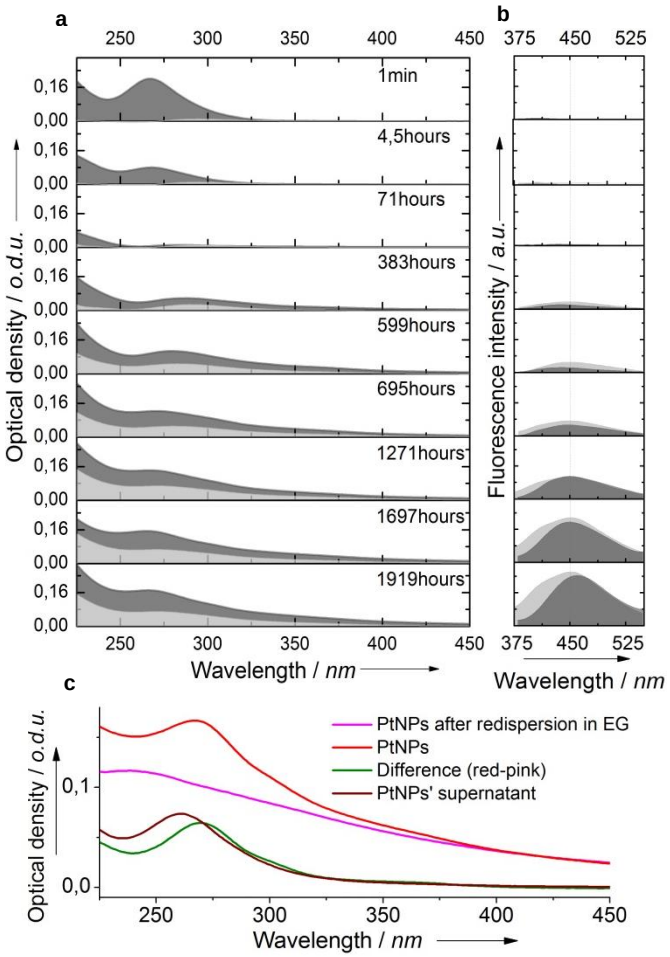

Figure 1. (**a**) Time evolution of absorption spectra measured at different time intervals during the synthesis of Pt NPs and a control solution containing only NaOH-EG. Light grey spectra represent 0.25M NaOH-EG, dark grey – the mixture of 4mM H_2PtCl_6-EG and 0.5M NaOH-EG. (**b**) Corresponding emission spectra (ex. 360nm). (**c**) Detailed investigation of different absorption bands appeared by the end of formation of Pt NPs after ~2000 hours. Red curve: PtNPs suspension; pink curve: Pt NPs re-dispersed in EG; brown curve: supernatant of Pt NP suspension; green curve: difference between red and pink curve (the peak shift most likely is related to a shift in OH^- concentration during the re-dispersion procedure) [5].

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It is important to note that the observed emission seems not to be related to Pt nanoclusters [6]. In figure 1b we clearly demonstrate that although the emission intensity constantly increases during the reaction, a similar behavior is observed in the control solution containing only NaOH-EG (but no Pt precursor). According to absorption and emission spectra shown in figure 1, it is obvious that not only the reaction mixture containing Pt salt (stored at RT and exposed to daylight), but also the EG itself undergoes complex chemical reactions after mixing with NaOH. We therefore assign the observed emission to the formation of organic byproducts, which should not be confused with Pt nanoclusters. Very recently, similar blue emission was observed in NaOH-EG reaction mixtures exposed to thermal treatment and the origin of the emission was assigned to the formation of nanometer sized carbon-dots [7].

A detailed investigation of the different absorption peaks appearing during NP synthesis is presented in figure 1c. To obtain a pure suspension, Pt NPs (synthesized by exposure to daylight at RT) were precipitated and re-dispersed in pure EG [5]. The re-dispersed NP suspension exhibits the typical absorption spectra of Pt NPs [7], whereas the difference spectrum between NPs in the original reaction mixture and re-dispersed NPs is similar to the Pt NPs' supernatant absorption spectrum. This demonstrates that the reaction products with main absorption peaks around 270 nm, 305 nm and 360 nm are not Pt NP-related and, according to [7], the latter two could be assigned to emissive carbon compounds.

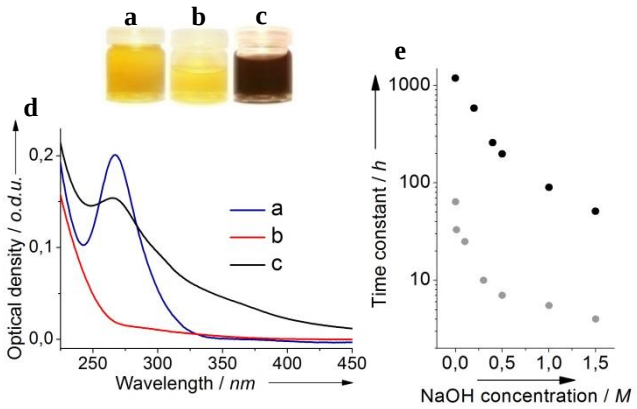

Figure 2. Photographs of (**a**) a freshly prepared reaction mixture of 4mM H_2PtCl_6-EG and 0.5M NaOH-EG; (**b**) a reaction mixture stored in the dark for ~2000 hours. (**c**) a reaction mixture exposed to daylight for ~2000 hours. (**d**) Representative absorption spectra of a, b and c. (**e**) Influence of daylight on the constant[1] of Pt salt (268 nm absorption peak) reduction while varying NaOH concentration. Grey dots represent samples exposed to daylight, black dots represent samples stored in dark.

Washing the Pt NPs and re-dispersing them in fresh EG improves the colloid stability[1e]. Their role in the particle formation is not clear, but it was observed that both the appearance of the emission and change in color of the colloidal suspensions occur at around the same time. Furthermore, in solutions that exhibit no emission, no formation of Pt NPs was observed either.

Next we investigated the role of light in the formation of the Pt NPs. Two samples of Pt NP synthesis reaction mixtures were stored in glass vials at RT during the whole synthesis process, one in dark, wrapped with aluminum foil, and the other exposed to daylight. Figure 2 a, b and c, show photographs of vials containing H_2PtCl_6-EG and NaOH-EG mixtures, freshly prepared, stored in the dark for ~2000 hours and exposed to daylight for ~2000 hours, respectively. No Pt NPs could be detected after precipitation in any of the reaction mixtures of 4mM H_2PtCl_6 with varying amounts of NaOH (0-1.5M) when the samples were stored in dark, see below. Figure 2d demonstrates that even though the $PtCl_6^{(-2)}$ complex reacts in dark over time, light seems to be essential for further reaction stages, i.e. the actual Pt NP formation. Only when daylight is present, Pt NPs form, as can be seen from the dark solution in Figure 2c, and the absorption spectrum in Figure 2d. Both light exposure and NaOH concentration critically affect the rate at which the $PtCl_6^{(-2)}$ complex disappears (see figure 2e). The time constant was almost 20 times faster, when reaction mixtures were exposed to light (grey dots) compared with a samples stored in dark (black dots).

To confirm that indeed Pt NPs are formed by exposing the reaction mixtures to daylight, the samples were analyzed by means of transmission electron microscopy (TEM) equipped with energy dispersive spectroscopy (EDS) as well as small angle X-ray scattering (SAXS). Upon exposing the reaction mixture to daylight, NPs of around 2 nm in size (see Fig. 3) were detected in the EG (by SAXS) and after washing and re-dispersion the colloidal suspension (by TEM). By comparison re-dispersion possible for samples kept in dark. EDS (see SI) confirmed that the observed NPs indeed are Pt. Comparing daylight induced NP formation at RT to our standard heat induced Pt NP synthesis [5] (see Fig. 3d), the former results in an average particle size that is slightly larger and exhibits a somewhat broader size distribution as a consequence of different precursor concentrations and slower reaction kinetics, see discussion of particle growth in SI. In previous work, UV-light induced Pt NP formation has been reported in combination with strongly binding ligands, which limit catalytic applications [8]. Using UV-light in a controlled way for unprotected NPs, we expect that the seed formation can be meticulously tuned by varying the irradiation intensity thus leading to very well-defined, tunable size distributions. Such investigations are currently under preparation.

[1] time of decay to 1/e of the initial optical density

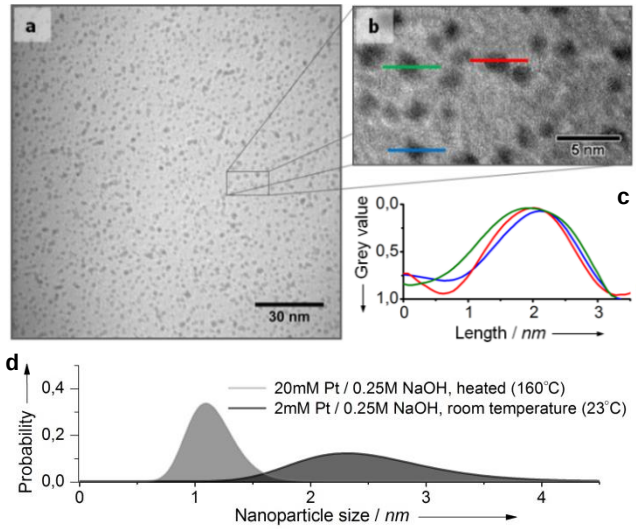

Figure 3. (**a**) Representative TEM micrographs of Pt NPs prepared by the polyol method at RT, (**b**) zoomed-in micrograph of a, (**c**) cross-sections of investigated (green, red and blue) Pt NPs, indicated on b. (**d**) Comparison of size distributions (obtained using SAXS) of Pt NPs prepared by the polyol method at RT and standard microwave assisted heating to 160°C, respectively.

We conclude that under the applied conditions of RT synthesis the exposure to light is crucial for the particle formation process. The use of light (more specific, UV light) to influence particle formation may lead to exciting new synthesis strategies for unprotected NPs. The observation of emission seems not to be related with the formation of Pt nanoclusters and claims of fluorescent metal clusters need to be cross-checked by performing the synthesis without metal precursor.

Experimental Section

Pt NPs were prepared based on a standard EG (polyol) synthesis method that we use in our group for the preparation of Pt based fuel cell catalysts [1a]. However a few modifications were introduced. In short, 4mM (1.64g/L) $H_2PtCl_6 \cdot xH_2O$ (99.9%, Alfa Aesar, Germany) precursor solution was prepared in EG (spectrophotometric grade, Alfa Aesar, Germany) and then mixed with an equal volume of 0.5M NaOH (98%, Alfa Aesar, Germany) in EG resulting in the reaction mixture with a final concentration of 2mM Pt precursor and 0.25M NaOH. In order to investigate the influence on synthesis temperature one of the reaction mixtures was stored in a glass vial in the laboratory at RT (~23°C). It was stored on the laboratory bench and thereby exposed to daylight and commercial fluorescent lightning tubes for the whole synthesis period (approximately 2000 hours). For comparison a standard Pt NP colloidal suspension was prepared using a reaction mixture containing 20mM of H_2PtCl_6 and 0.25M NaOH by heating to 160°C for 3 minutes under constant stirring in a microwave synthesis apparatus (CEM SP Discover, USA). As a result of these treatments the precursor solutions turned dark brown indicating that Pt NPs were formed [1c]. As reference, the same procedure as with first sample was performed, but instead of exposing it to daylight, it was kept in the dark by wrapping the vial in aluminum foil.

For UV-VIS absorption and fluorescence emission measurements small amounts of colloidal suspensions were taken out from the reaction mixtures and diluted with pure EG for up to 100 times. Pure EG was used as a baseline for both described spectroscopic methods (UV-VIS absorption and fluorescence emission measurements), performed using Lambda 1050 UV/VIS/NIR absorption spectrophotometer (Perkin Elmer, USA) and Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, USA) .

For TEM measurements the Pt NPs were washed with 1 M HCl and re-dispersed in ethanol (max. 0.01% H_2O, Merck Millipore, Germany) according to [1a, 1c]. The colloidal solution was mixed with aqueous solution of 1M HCl in a volume ratio of around 1:3. Then a dark brown precipitate was centrifuged (Sigma 2-5, Germany) at 4000 rpm for 5 minutes. This particle separation process was repeated twice in order to remove remaining EG. Thereafter the Pt precipitate was re-dispersed in pure ethanol and diluted ca. 50 times. Small drops of solution were placed on carbon film coated copper grids, drained and dried in air for ~18 hours. The images of Pt NPs were obtained by Tecnai T20 G2 transmission electron microscope (Philips FEI, Oregon, USA) operated at 200kV. For confirming that the imaged NPs are Pt, EDS was performed in the TEM at different sample spots.

Small Angle X-ray Scattering (SAXS) measurements were performed using a SAXSLab instrument (JJ-X-ray, Denmark) equipped with a Rigaku 100 XL+ micro focus sealed X-ray tube and a Dectris 2D 300 K Pilatus detector, by placing a small amount of re-dispersed Pt NPs (in EG) into a liquid sample holder. The analysis was performed according to [1a].

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Keywords: Nanoparticles • colloidal synthesis • steady state absorption and fluorescence spectroscopy • Platinum

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